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16. ABSTRACT

Analytical techniques have been developed for the collection and determination of gas phase dimethyl sulfate and monomethyl sulfuric acid in the flue lines and plumes of power plants and in the ambient atmosphere. The techniques involve the collection of the gas phase species in denuders which are selective for monomethyl sulfuric acid or which collect both dimethyl sulfate and monomethyl sulfuric acid, and determination of the deposition pattern of the collected alkyl sulfates in the denuder. In addition, both dimethyl sulfate and monomethyl sulfuric acid are collected in filter pack, sorbent bed combinations which allow for the separate determination of both dimethyl sulfate and monomethyl sulfuric acid or for their joint collection and determination. Monomethyl sulfuric acid is determined by ion chromatography. Dimethyl sulfate is determined either by ion chromatography or by gas chromatography, depending on the collection device used. The sampling and analysis techniques allow for the determination of both dimethyl sulfate and monomethyl sulfuric acid by two independent procedures with an accuracy of about ±10% and a detection limit of from 2 to 10 nanomoles. Dimethyl sulfate is a known mutagen and probable carcinogen. Data obtained with the sorbent bed sampling techniques indicate that gas phase dimethyl sulfate is present in the flue line of a coal-fired steam plant.

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JOURNAL ARTICLE

Determination of Gas-Phase Dimethyl Sulfate and Monomethyl Hydrogen Sulfate†

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■ Analytical techniques have been developed for the collection and determination of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate. The techniques include the collection of the gas-phase species in diffusion denuders that are selective for monomethyl hydrogen sulfate or that collect both dimethyl sulfate and monomethyl hydrogen sulfate. Dimethyl sulfate and monomethyl hydrogen sulfate are also collected in filter pack adsorbent bed combinations which allow for the separate determination of both dimethyl sulfate and monomethyl hydrogen sulfate or for their joint collection and determination. The sampling and analysis techniques thus allow for the determination of both di- and monomethyl sulfates each by two independent procedures with a detection limit of 2–10 nmol by ion chromatography. Data obtained with the adsorbent bed sampling techniques indicate that gas-phase dimethyl sulfate is present at very low concentrations in the flue line of a coal-fired steam plant.

Introduction

We have previously reported the presence of dimethyl and monomethyl sulfate in airborne particulate matter and in fly ash from coal- and oil-fired power plants (*1–5*). These previous studies (*1, 3, 4*) also indicate that dimethyl sulfate in particles in the plumes of both oil- and coal-fired power plants increases with plume age. Because of the known mutagenicity of dimethyl sulfate (*6, 7*), sensitive analytical techniques are needed to determine gas-phase dimethyl sulfate and monomethyl hydrogen sulfate.

The collection of dimethyl sulfate and monomethyl hydrogen sulfate from the gas phase may be complicated because of reactions such as

$$(CH_3O)_2SO_2 + H_2O = (CH_3O)SO_3H + CH_3OH \quad (1)$$

$$(CH_3O)SO_3H + H_2O = H_2SO_4 + CH_3OH \quad (2)$$

$$2(CH_3O)SO_3H = (CH_3O)_2SO_2 + H_2SO_4 \quad (3)$$

Since each of these reactions is expected to occur in the atmosphere, more than one analytical technique for the collection and determination of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate is desired to ensure that these reactions are avoided during sample collection and analysis.

This report describes the development and validation of procedures for the collection and determination of both dimethyl sulfate and monomethyl hydrogen sulfate in the gas phase using a variety of diffusion denuder tube and sorbent bed collection systems.

Experimental Section

Preparation of Dimethyl Sulfate and Monomethyl Hydrogen Sulfate Standards. Potassium monomethyl sulfate is available (Eastman) in reagent grade. Determination by ion chromatography (*5*) of both sulfate and monomethyl sulfate in solutions of potassium monomethyl sulfate prepared by weight indicated that the purity of the commerical sample used in this study was 94% by weight. Aqueous solutions of the potassium monomethyl sulfate were stable for at least 6 months with no measurable change in composition. Samples of dimethyl sulfate were prepared by vacuum distillation of the commercial material (Mallinckrodt) at 80 °C. The concentrations of both dimethyl sulfate and monomethyl sulfate in freshly prepared aqueous solutions of the distilled sample were determined by ion chromatography (*3, 5*). The distilled samples had a purity of about 98% by weight, with the impurity being monomethyl sulfate. The freshly distilled samples could be stored at room temperature for a few weeks before measurable decomposition occurred. Monomethyl hydrogen sulfate is not available commercially. Monomethyl hydrogen sulfate was prepared from the potassium monomethyl sulfate salt by cation exchange of K^+ for H^+ using Dowex ion-exchange resin in the acid form. Twenty-five milliliters of the resin was packed in a column and thoroughly washed with anhydrous methanol. A saturated solution of $K(CH_3O)SO_3$ in methanol was then put on the column and eluted with methanol, the $(CH_3O)SO_3H$ from the column being detected by the measurement of acidity. The solvent was then rapidly removed in a Rotovac at room temperature with no heating of the sample. The resulting viscous liquid was stored at −80 °C until used. Ion chromatographic analysis of the samples indicated that the purity of monomethyl hydrogen sulfate prepared by this procedure varied from 70% to 95%. The impurities were dimethyl sulfate and sulfuric acid. The monomethyl hydrogen sulfate slowly disproportionated according to eq 3 even at −80 °C. At room temperature, the half-life of reaction 3 for the liquid monomethyl hydrogen sulfate was about 8 h. As a result, samples of liquid monomethyl hydrogen sulfate used to generate $(CH_3O)SO_3H(g)$ were used immediately after removal from the −80 °C storage chamber.

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Gas-phase dimethyl sulfate and monomethyl hydrogen sulfate were both generated from the corresponding liquid by passing pure N_2 or Ar over the liquid to sweep away the vapor in equilibrium with the liquid. In all experiments used to evaluate the collection of gas-phase methyl sulfates by denuders or adsorbent beds, a filter was placed between the gas-phase generator and the collector to remove any aerosol present.

Denuders. Field experiments done in several urban areas by Durham et al. (*8*, *9*) have shown that a nylon denuder collects a gas which, after storage of the denuder for several weeks to months, produces sulfate upon ion chromatographic analysis of aqueous extracts of the denuder. The sulfate deposition patterns indicate that the diffusion coefficient, D_0, of the collected gas is the same as that expected for dimethyl sulfate, $D_0 = 0.073$ cm^2/s, or monomethyl hydrogen sulfate, $D_0 = 0.081$ cm^2/s (*8*). It was shown that the gas was not SO_2 or H_2S. Most significantly, the concentration of the gaseous sulfur compound inferred from these denuder measurements was usually comparable to the concentrations of particulate sulfate. Similar concentrations of an unidentified gas-phase organic sulfur compound in urban atmospheres have been inferred from experiments with an activated carbon denuder (*10*). We have studied the collection of gas-phase dimethyl sulfate, monomethyl hydrogen sulfate, combinations of dimethyl sulfate and monomethyl hydrogen sulfate, and SO_2 by nylon denuders. In the course of these experiments, we found that the paper dividers supplied with the nylon strips were selective for the collection of monomethyl hydrogen sulfate. Therefore, the collection of dimethyl sulfate, monomethyl hydrogen sulfate, and SO_2 by the paper dividers was also studied. Diffusion-denuder tubes were made by placing rolled tubes of nylon-membrane sheets (Membrana) or the paper sheets inside Teflon carrier tubes. The inside diameter of the Teflon tube was either 0.78 or 0.70 cm. Six 10-cm long nylon or paper tubes were used in each denuder.

Laboratory Studies with the Denuders. The collection pattern of dimethyl sulfate, monomethyl hydrogen sulfate, and SO_2 by both the nylon and paper denuders in the absence of particles was determined. The gas-phase dimethyl sulfate and monomethyl hydrogen sulfate were generated by passing N_2 or Ar over the pure liquids or a mixture of the two liquids. In some cases, the collection of dimethyl sulfate and monomethyl hydrogen sulfate by the paper denuder in the presence of H_2O vapor was also studied. In these experiments, the gas-phase alkyl sulfate was mixed with an air stream of equal flow rate containing H_2O(g) obtained by flowing air over water. In all cases, any particles in the air stream were removed by using an acid-washed quartz filter, and the resulting gas was pulled through the denuder at a flow rate of 1.5 L/min. After the denuder, dimethyl sulfate or monomethyl sulfate was collected with two nylon filters or an aqueous bubbler. A basic, aqueous bubbler was used to collect SO_2. The quartz prefilter, the 10-cm denuder sections, and the nylon filters were all immediately extracted with water at 25 °C in an ultrasonic bath for 15 min. The extracted monomethyl hydrogen sulfates, sulfate, and SO_2 (as sulfate) were analyzed directly by ion chromatography. In all cases, the ion chromatographic determination was repeated after 24 h to determine the presence of any dimethyl sulfate in the extract solution by its hydrolysis to monomethyl sulfate (*3*, *5*). Blank runs indicated that sulfate was present in both the nylon, 8.5 ± 4.5 nmol/section, and paper, 84 ± 22 nmol/section, sections. No diemthyl sulfate or monomethyl sulfate was found in the blank determinations.

Table I. Sampling System Used for the Collection of Gas-Phase Dimethyl Sulfate and Monomethyl Hydrogen Sulfate in the Flue Line of a Coal-Fired Steam Plant

sequential parts of sampling system	compounds collected[a]	species determined
(1) quartz filter	DMS, MSA in particles	$(CH_3O)_2SO_2$, $CH_3OSO_3^-$, SO_4^{2-}
(2) glass wool plug	H_2SO_4, MSA, DMS	$(CH_3O)_2SO_2$, $CH_3OSO_3^-$, SO_4^{2-}
(3) XAD-II bed	DMS	$(CH_3O)_2SO_2$, $CH_3OSO_3^-$, SO_4^{2-}
(4) XAD-II bed	DMS	$(CH_3O)_2SO_2$, $CH_3OSO_3^-$, SO_4^{2-}
(5) nylon filters	MSA	$CH_3OSO_3^-$, SO_4^{2-}
(6) glass wool plug	H_2SO_4, MMS, DMS	$(CH_3O)_2SO_2$, $CH_3OSO_3^-$, SO_4^{2-}
(7) NaOH scrubber	SO_2	SO_4^{2-}

[a] DMS is dimethyl sulfate, and MSA is monomethyl hydrogen sulfate.

Laboratory Studies with Sorbent Materials. The collection of gas-phase dimethyl sulfate, monomethyl hydrogen sulfate, and SO_2 by sorbent beds containing XAD-II (Rohm and Haas), poly(vinylamine) (PVA), poly(ethylenimine) (PEI), poly(vinylpyridine) (PVP), or Melamine (*11*) was studied as a function of temperature from 25 up to 125 °C. The collection of dimethyl sulfate and monomethyl hydrogen sulfate by 47-mm nylon filters was also studied. The gas-phase species were generated in the same manner as described for the denuder experiments. In some cases, two sorbent beds or two nylon filters were placed in series to determine collection efficiency. Any sulfur compounds passing the sorbents were collected in an aqueous bubbler. An acid-washed quartz filter was placed before the sorbent beds to remove any particles. The collected samples were all extracted with water at 25 °C in an ultrasonic bath for 15 min and dimethyl sulfate, monomethyl hydrogen sulfate, sulfate, and SO_2 determined by ion chromatography as described above. Some XAD-collected dimethyl sulfate samples were exposed to ammonia (*3*) before being extracted with water. In addition, dimethyl sulfate was directly determined in some XAD sorbent samples by direct probe mass spectroscopy.

Absorption by Sulfuric Acid Aerosol. Since these analytical techniques are intended to be used in flue line sampling where H_2SO_4 aerosol may be formed if the temperature of the sampled flue line is reduced, the absorption of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate by H_2SO_4(l) was also studied. In these experiments, a quartz filter was wetted with an aqueous H_2SO_4 solution and air-dried. Gas-phase dimethyl sulfate and monomethyl hydrogen sulfate were generated in an N_2 stream and either filtered and passed over the H_2SO_4-containing filter or mixed with an air stream saturated with H_2O(g) at 25 °C, filtered, and passed over the H_2SO_4-containing quartz filter. Experiments were preformed with the quartz filter and incoming gas stream at 25 or 75 °C. The moles of gas-phase alkyl sulfate passed through the filter was about 100 times the number of moles of H_2SO_4 on the quartz filter. The dimethyl sulfate or monomethyl hydrogen sulfate passing the H_2SO_4 wetted quartz filter was trapped in a H_2O bubbler. The bubbler and quartz filter were analyzed for dimethyl sulfate, monomethyl hydrogen sulfate, and sulfuric acid by ion chromatography as described earlier. The acidity of the aqueous extract of the quartz filter was determined by pH measurement.

Field Trial Experiments. The collection of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate was tested in field experiments. The configuration of the

Table II. Collection Efficiency of Sorbent Traps for Gas-Phase Dimethyl Sulfate and Monomethyl Hydrogen Sulfate

		efficiency, %		concentration, μmol/m³		total sampled, μmol	
sorbent	T, °C	$(CH_3O)_2SO_2$	CH_3OSO_3H	$(CH_3O)_2SO_2$	CH_3OSO_3H	$(CH_3O)_2SO_2$	CH_3OSO_3H
XAD-II	25	99.3 ± 1.0	9.4 ± 6.6	13–166	5–130	3–31	0.3–12
	60	78.7	10.2	840	50	38	2.2
	75	0.02		80–166		1–31	
PVA	25	0.3 ± 0.3	13 ± 20	15	4–900	50	0.2–135
PEI	25	64 ± 28	16.7 ± 0.2	5–10	2–8	0.5–1.0	0.4
	75	18	4.4 ± 6.1	60	14–36	2.7	0.6–1.2
PVP	25	19 ± 19	67 ± 24	2–68	3–70	0.1–14	0.2–70
	75	0.1 ± 0.2	9 ± 11	3–1070	0.3–2	23–48	0.3–1.9
	125	<0.1	8.2 ± 2.3	7–480	1–55	0.4–30	2–13
Melamine	25	<0.1	6 ± 100[a]	44–100	0.6–11	2–5	0.03–0.5
	75		20 ± 80[a]		7–22		0.3–1.0
	125		60		0.6		0.1
nylon	25	75 ± 13	99.1 ± 0.7	7	3	0.2	0.1

[a] Efficiency is a function of total amount sampled. Data indicate that the absorption capcity of the 3-mL sorbent bed for CH_3OSO_3H is about 60 nmol at 25 °C, 200 nmol at 75 °C, and 20 nmol at 125 °C.

sampling system used is given in Table I. Samples were collected from the flue line of a small coal-fired heating plant (*5*) with a flue line temperature of 140 °C. As indicated in Table I, particulate matter was removed with an acid-washed quartz filter heated to the flue line temperature. The exiting gases were then mixed with an equal volume of clean air to reduce the dew point, cooled to 55 °C in a thermostated box, and passed sequentially through a glass wool plug to remove condensed H_2SO_4, two XAD-II resin beds of 3-mL capacity each, and a nylon filter. The gases were then cooled to ambient temperature and passed through a second glass wool plug followed by a 10 mM NaOH(aq) scrubber. Sample flow rate was 20 L/min. The quartz filter with the particulate matter sample was divided in half, and half was exposed to NH_3(g) to allow for the determination of dimethyl sulfate in the collected sample (*3*). The various filter, glass wool, and resin trap samples were immediately extracted with H_2O and analyzed for sulfate and monomethyl sulfate by ion chromatography (*3, 5*). These analyses were repeated on a second aliquot of the extracts after 24 h.

Results

The results obtained on the collection of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate by the various sorbent beds and nylon filters are given in Table II. The results of the studies on the collection of dimethyl sulfate and monomethyl hydrogen sulfate by H_2SO_4 are given in Table III. The denuder deposition patterns for collection of dimethyl sulfate and monomethyl hydrogen sulfate by nylon denuders and for collection of monomethyl hydrogen sulfate by the paper denuder are given in Table IV. Dimethyl sulfate was not collected by the paper denuder, either in the presence or in the absence of H_2O in the gas phase. These experiments included studies where the paper denuder was equilibrated with H_2O(g) for up to 4 h before the dimethyl sulfate was passed through the denuder. The results of the studies on the collection of SO_2(g) by the paper denuder, XAD sorbent bed, or nylon are summarized in Table V. The results of the trial experiments in the flue line of a coal-fired heating plant are given in Table VI.

Discussion

Sorbent Beds. The results given in Table II show that dimethyl sulfate is quantitatively collected by XAD-II resin at ambient temperatures. However, the collection efficiency of XAD-II for dimethyl sulfate is poor above about 50 °C. This is also demonstrated by the direct probe mass spectrometric analysis of XAD-II beads exposed to gas-phase dimethyl sulfate as shown in Figure 1. As the data in Figure 1 indicate, dimethyl sulfate is released from the XAD-II beads during heating of the sample in a vacuum beginning at about 50 °C with a maximum at about 70 °C. The major peak is dimethyl sulfate as shown by the mass spectrum in Figure 1. The small shoulder present in the total ion plot at about 50 °C is due to monomethyl hydrogen sulfate. Ion chromatographic analyses of the XAD-II after exposure to dimethyl sulfate showed that the dimethyl sulfate is adsorbed and extracted into H_2O without decomposition or loss. During a 24-h period, the extracted dimethyl sulfate was quantitatively hydrolyzed to monomethyl sulfate in the laboratory experiments. Analysis of some XAD sorbent bed samples used to sample air in the Los Angeles basin (*12*) indicated that, when coextracted with other organic compounds, dimethyl sulfate reacted to form both monomethyl sulfate and sulfate. It was anticipated that exposure of the XAD-collected dimethyl sulfate to NH_3(g) before extraction would convert the dimethyl sulfate to monomethyl sulfate which could be analyzed by IC immediately after aqueous extraction. However, IC analysis of dimethyl sulfate on XAD-II after exposure to NH_3(g) followed by extraction with water indicated that only about one-third of the

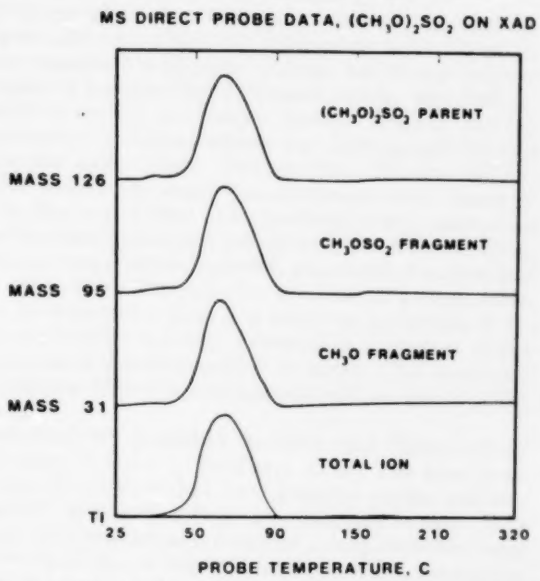

Figure 1. Direct probe temperature programmed mass spectral determination of dimethyl sulfate adsorbed on XAD-II.

Table III. Collection of Gas-Phase Dimethyl Sulfate and Monomethyl Hydrogen Sulfate by Sulfuric Acid on a Quartz Filter

T, °C	H_2O present	collected mol:mol of H_2SO_4		apparent Henry's law K, (mol/mol H_2SO_4)/(nmol/m^3)	
		$(CH_3O)_2SO_2$	CH_3OSO_3H	$(CH_3O)_2SO_2$	CH_3OSO_3H
25	no	0.11 ± 0.07	<0.04	0.26 ± 0.08	<0.2
	yes[a]	0.17 ± 0.06	0.29 ± 0.04	0.40 ± 0.04	1.5 ± 1.2
75	no	0.17 ± 0.04	<0.03	0.53 ± 0.11	<0.1
	yes[a]	<0.03	<0.03	<0.06	<0.09

[a] Concentration of $H_2O(g) \approx 30$ mbar; see text.

XAD-II-adsorbed dimethyl sulfate was converted to monomethyl sulfate upon exposure to $NH_3(g)$. The collection efficiency values given in Table II for dimethyl sulfate are based on the determination of dimethyl sulfate as monomethyl sulfate by ion chromatography after hydrolysis. The capacity of the XAD-II resin for dimethyl sulfate is at least 10 μmol of dimethyl sulfate/mL of XAD-II resin.

The XAD-II resin retains a small percentage of any monomethyl hydrogen sulfate gas passed through the bed. The measured collection efficiency at 25 °C varied from 2 to 22% and was directly related to the concentration of gas-phase monomethyl hydrogen sulfate, suggesting that the binding site for monomethyl hydrogen sulfate has a small equilibrium constant for the binding. It can be expected that, at ambient concentrations of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate, XAD-II will selectively collect dimethyl sulfate and pass monomethyl hydrogen sulfate. The data obtained at 60 and 75 °C suggest that, at elevated temperatures, some of the collected dimethyl sulfate is converted to monomethyl sulfate on the XAD-II resin. For example, the collection and analysis of a sample of dimethyl sulfate on XAD-II at 25 °C followed by an aqueous bubbler indicated that the purity of the generated gas-phase sample was 95% dimethyl sulfate and 5% monomethyl sulfate. When the same sample was first passed through an XAD-II resin bed at 75 °C, the collected sample was 27% monomethyl sulfate. This conversion of some dimethyl sulfate to monomethyl sulfate on XAD-II at elevated temperatures is consistent with the direct probe mass spectral data shown in Figure 1.

None of the other resin beds studied, with the exception of Melamine, was quantitatively selective for either dimethyl sulfate or monomethyl hydrogen sulfate. As indicated in Table II, Melamine will selectively sorb monomethyl hydrogen sulfate in the presence of dimethyl sulfate, but the absorption capacity is low, about 20 nmol/mL at 25 °C. In addition, the concentration of sulfate in samples exposed to monomethyl hydrogen sulfate was always slightly higher than the blank values, indicating some of the monomethyl sulfate is converted to sulfate during the sampling. Since this conversion process may be catalyzed by unknown compounds present in the atmosphere and since Melamine is expected to scrub $SO_2(g)$ which would be converted to sulfate (*11*), Melamine was not considered to be a good sorbent for the collection of monomethyl hydrogen sulfate.

It was expected that the PVA resin would be methylated by dimethyl sulfate to form the methylamine polymer and monomethyl sulfate. However, the laboratory experiments indicated that this methylation reaction was not quantitative. As indicated in Table II, little dimethyl sulfate was found in aqueous extracts of the PVA polymer after exposure to dimethyl sulfate, indicating that most absorbed dimethyl sulfate had reacted with the polymer. However, when the PVA was exposed to dimethyl sulfate, the aqueous bubbler after the PVA contained both dimethyl sulfate and monomethyl sulfate, thus showing that the methylation process was not quantitative. The data show that only about 25% of the dimethyl sulfate reacted with the PVA resin bed at 25 °C. In addition, experiments with both dimethyl sulfate and monomethyl hydrogen sulfate indicated that both dimethyl sulfate and monomethyl hydrogen sulfate are poorly retained by PVA.

Both gas-phase dimethyl sulfate and monomethyl hydrogen sulfate are effectively collected by nylon filters. In some experiments dimethyl sulfate, which is present in samples of monomethyl hydrogen sulfate, was first removed by passing the sample through XAD-II, and the monomethyl hydrogen sulfate was then passed through sequential nylon filters. The gas-phase monomethyl hydrogen sulfate was nearly quantitatively (99%) removed by the first nylon filter. The products of this adsorption of monomethyl hydrogen sulfate by nylon filters in these laboratory experiments was 99% monomethyl sulfate and only 1% sulfate. The collection efficiency of a single nylon filter for dimethyl sulfate as a lower but acceptable 77%. Dimethyl sulfate was not recovered as a product of the adsorption of dimethyl sulfate by nylon. The recovered material was 82 ± 8% monomethyl sulfate and 18 ± 8% sulfate.

Removal of Dimethyl Sulfate and Monomethyl Hydrogen Sulfate by Sulfuric Acid. The data given in Table III indicate that both dimethyl sulfate and monomethyl hydrogen sulfate are sparingly soluble in a sulfuric acid droplet, and it can be anticipated that some alkyl sulfate may be removed from the gas to the aerosol phase if aerosol sulfuric acid is allowed to form during sampling in a flue line. The results indicate that monomethyl sulfate is only removed if the temperature is low and water is present. Presumably the water results in an increase in the filter-bound liquid due to hydration of sulfuric acid with a corresponding decrease in the acidity of the liquid on the filter. This results in increased solubility of the monomethyl sulfate. The effects of temperature and gas-phase water concentration on the removal of dimethyl sulfate by sulfuric acid is not clear from the data presented in Table III. The concentration of gas-phase dimethyl sulfate was varied by a factor of 5 over the concentration range 100–500 μmol/m^3 for the experiments at 25 °C where apparent Henry's law constants are given. The fact that this apparent constant did not vary with changes in the gas-phase concentration suggests that the system was in equilibrium. This apparent Henry's law constant can be used to predict the collection of gas-phase dimethyl sulfate by a sulfuric acid aerosol at lower concentrations of gas-phase dimethyl sulfate. For example, experiments on the collection of gas-phase dimethyl sulfate in the flue line of a coal-fired heating plant (see Table VI) indicate that the mole ratio of $SO_3(g)$ to gas-phase dimethyl sulfate was about 70 and that the concentration of gas-phase dimethyl sulfate in the sampled air stream was about 0.1 nmol/m^3. Under these conditions, apparent Henry's law constants given in Table III would predict that

Table IV. Collection of $(CH_3O)_2SO_2$(g) and CH_3OSO_3H(g) by Nylon- and Paper-Lined Denuder Tubes[a]

denuder	section no.	G_j, nmol/section						
paper, MSA	1	869 ± 8[c]	55 ± 5[b]	47 ± 5[b]	174 ± 9[c]	110 ± 8	577 ± 8	101 ± 8
	2	350 ± 8	49 ± 5	27 ± 5	57 ± 8	138 ± 8	299 ± 8	80 ± 8
	3	112 ± 8	39 ± 5	20 ± 5	112 ± 8	103 ± 8	230 ± 8	78 ± 8
	4	97 ± 8	13 ± 5	18 ± 5	102 ± 8	49 ± 8	110 ± 8	28 ± 8
	5	52 ± 8	20 ± 5	0 ± 5	29 ± 8	39 ± 8	91 ± 8	22 ± 8
	6	42 ± 8	13 ± 5	2 ± 5	18 ± 8	26 ± 8	121 ± 8	
	passing	110 ± 20	36 ± 20	78 ± 20	28 ± 20	53 ± 20	152 ± 20	
	total	1632	225	192	520	517	1579	
	% MMS[d]	2.4	0	0	29	7	50	22
	flow, L/min	1.50	1.50	1.50	1.50	1.50	1.54	1.54
	D_0, cm^2/s	0.102 ± 0.023	0.070 ± 0.014	0.092 ± 0.018	0.080 ± 0.030	0.092 ± 0.030	0.108 ± 0.016	0.071 ± 0.022
	T_j, nmol	993 ± 54	303 ± 10	200 ± 7	624 ± 110	806 ± 40	866 ± 40	551 ± 24
nylon, MSA	1	91 ± 5	36 ± 5	38 ± 3				
	2	107 ± 5	24 ± 5	25 ± 3				
	3	61 ± 5	10 ± 5	14 ± 3				
	4	52 ± 5	8 ± 5	7 ± 3				
	5	22 ± 5	12 ± 5	7 ± 3				
	6	12 ± 5	5 ± 5	3 ± 3				
	passing	90 ± 20	8 ± 5	4 ± 3				
	total	435	103	98				
	flow, L/min	1.41	1.50	1.50				
	D_0, cm^2/s	0.065 ± 0.022	0.093 ± 0.016	0.094 ± 0.024				
	T_j, nmol	585 ± 58	140 ± 6	125 ± 5				
nylon, DMS	1	94 ± 3	176 ± 8[c]	46 ± 3	94 ± 3			
	2	58 ± 3	107 ± 8	56 ± 3	65 ± 3			
	3	44 ± 3	90 ± 8	30 ± 3	51 ± 3			
	4	33 ± 3	39 ± 8	22 ± 3	33 ± 3			
	5	35 ± 3	89 ± 8	11 ± 3	23 ± 3			
	6	17 ± 3	68 ± 8	3 ± 3	12 ± 3			
	passing	107 ± 10	105 ± 20	17 ± 3	107 ± 3			
	total	388	674	168	385			
	% MMS[d]	71	87					
	flow, L/min	1.50	1.68	1.50	1.50			
	D_0, cm^2/s	0.078 ± 0.009	0.070 ± 0.017	0.097 ± 0.012	0.065 ± 0.007			
	T_j, nmol	418 ± 9	640 ± 5	280 ± 3	395 ± 3			

[a] Data analyzed by weighted least-squares fit to eq 4. [b] H_2O present at ≈ 15 mbar. [c] The carrier gas was Ar. [d] % MMS = percent of total sulfur in denuder present as monomethyl sulfate after extraction with H_2O. [e] Data obtained at 95 °C.

only about 2% of the gas-phase dimethyl sulfate would be removed by formation of a sulfuric acid aerosol from the SO_3(g) during sampling. This prediction agrees with the results obtained in the field where the amount of dimethyl sulfate collected in a controlled temperature condensation (glass wool plug) collection of SO_3(g) as H_2SO_4 after removal of particulate matter at the flue line temperature (quartz filter) was 3% of the total (Table VI).

Collection of Dimethyl Sulfate and Monomethyl Hydrogen Sulfate by Diffusion Denuders. In the separation of a gas species from an aerosol in a diffusion denuder, it is usually assumed that the diffusing gas reacts with an efficiency of 1 upon collision with the wall of the denuder. If this condition holds, the deposition pattern of the gas in the cylindrical denuder can be calculated by using the Gormley–Kennedy (*13*) equation as formulated by Durham and Spiller (*14*):

$$G_j = 0.819T_i[e^{(3.657D_i dt_x/r^2)} - 1]e^{(-3.657D_i t_j/r^2)}, \quad j > 1 \quad (4)$$

where G_j = amount deposited in the jth section of the denuder, T_i = total amount that entered the denuder, D_i = the gas diffusion coefficient at the experimental conditions, dt_x = axial displacement time for transport through equal length sections of the denuder, t_j = axial displacement time for travel of the gas from the inlet through section j, and r = the radius of the cylindrical denuder. Conversely, the diffusion coefficient of a gas collected in a diffusion denuder can be calculated by using eq 4 and data on the fractional penetration of gases through the denuder. The gas-phase diffusion coefficients for dimethyl sulfate and monomethyl hydrogen sulfate have been estimated to be D_0 : 0.073 and 0.081 cm^2/s, respectively, at 1 bar and 25 °C (*8*). We have evaluated our data for the collection of gas-phase monomethyl hydrogen sulfate by both the paper and nylon denuders and for the collection of gas-phase dimethyl sulfate by the nylon denuder (corrected to a D_0 value valid at 1 bar and 25 °C) by weighted least-squares fit of the data to eq 4. The results, summarized in Table IV, indicate that eq 4 describes the collection of these two gases. Examples of our results with the nylon denuder are illustrated in Figure 2 for collection of both gaseous dimethyl sulfate and monomethyl hydrogen sulfate. The average experimental D_0 values obtained for dimethyl sulfate and monomethyl hydrogen sulfate are 0.078 ± 0.014 and 0.087 ± 0.014 cm^2/s, respectively, in good agreement with the predicted values (*8*). The D_0 values for monomethyl hydrogen sulfate obtained by the two denuders are in agreement. These results show that the paper denuder can be used to collect monomethyl hydrogen sulfate and the nylon denuder can be used to collect dimethyl sulfate plus monomethyl hydrogen sulfate. The identity of the species collected can be confirmed by the experimentally determined D_0 value.

The collection of dimethyl sulfate and monomethyl hydrogen sulfate can also be confirmed by the species determined to be present in the denuder. When dimethyl sulfate is collected by the nylon denuder (or by a nylon filter), it is mainly converted to monomethyl sulfate with some sulfate ion also being present (Table IV). Monomethyl sulfate is also expected to be the dominant product

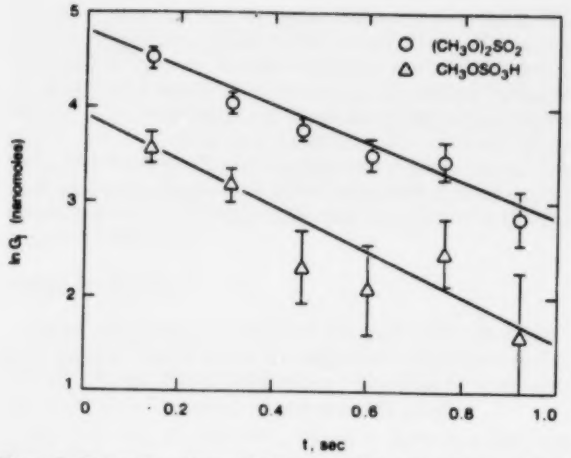

Figure 2. Deposition pattern of dimethyl sulfate (O) and monomethyl hydrogen sulfate (Δ) in a nylon diffusion denuder.

V. Collection of SO_2(g) by Nylon, Paper, and XAD-II Sampling Systems

$[SO_2]$, μmol/m³	collection system	% of total SO_2 collected[a] first trap	% of total SO_2 collected[a] second trap	nmol of SO_2 collected first trap	nmol of SO_2 collected second trap
1817	XAD-II	0.015	0.016	32	34
	nylon filter	0.028		62	
74	XAD-II	0.24	0.34	21	30
	nylon filter	0.42		37	
1499	paper denuder	0.23	0.35	414	635
	nylon filter	0.018		32	
323	paper denuder	0.15	0.023	60	9
	nylon filter	0.003		1	
27	nylon denuder	7.74	6.89	94	77
		7.30[b]	7.27[b]	76[b]	70[b]
	nylon filter	5.20	5.03	47	43
3	nylon denuder	0.83	0.36	2.3	1.0
		0.18[b]	0.55[b]	0.5[b]	1.5[b]
	nylon filter	1.00	1.42	2.7	3.8

[a]Calculated based on total SO_2 passing the trap. [b]Third and fourth sections of the nylon denuder.

resulting from the collection of monomethyl hydrogen sulfate by nylon. Apparently dimethyl sulfate and, to a lesser extent, monomethyl sulfate can methylate the nylon surface upon adsorption. The collection of monomethyl hydrogen sulfate by the paper denuder is expected to be due to adsorption of the acid on basic sites and not to methylation of the surface since dimethyl sulfate did not react with the paper denuder. The species found after adsorption of monomethyl hydrogen sulfate by the paper denuder was, however, a mixture of monomethyl sulfate and sulfate ion (see Table IV). Evidently, the monomethyl sulfate is not stable on the paper surface and can hydrolyze to sulfate.

Interference by SO_2(g). The various experiments on the adsorption of SO_2(g) by the paper denuder, nylon denuder, nylon filter, or a 3-mL sample of XAD-II (Table V) indicate that a small percentage of the total SO_2 is collected by each of these media and analyzed as sulfate. The collection of SO_2(g) by sequentially placed diffusion denuder adsorbent beds indicated that the collection was nearly independent of position. This was expected since only a small percentage of the total was collected. These results indicate that the collection efficiency of the surface for SO_2(g) is much less than 1. The collection efficiency was, however, not linearly related to the SO_2(g) concentration. For 47-mm nylon filters, and the nylon denuder strips, the adsorption capacity for SO_2(g) appears to be about 45 ± 12 and about 75 nmol of SO_2(g), respectively. The percent of total SO_2(g) that can be expected to be collected by a nylon filter or denuder section at ambient SO_2(g) concentrations is less than 5% of the total SO_2(g). Similar results have been obtained by other investigators (*5*, *6*). The absorption capacity of the XAD-II resin is about 10 nmol of SO_2(g)/mL of resin, and the amount of SO_2(g) that will be collected at ambient conditions will be less than 0.5% of the total SO_2(g). The absorption capacity of the paper denuder sections for SO_2(g) is high, but the percent of the total SO_2(g) that would be expected to be collected under ambient conditions would be less than 0.1% on the basis of the limited results given in Table V. For the nylon filter or the sorbent beds, the collection of SO_2(g) can be checked in field experiments by sequential collection on two filter or resin beds. The presence of this possible artifact for the collection of the alkyl sulfate compounds by the denuders may be checked by the positioning of a short denuder after the XAD-II resin beds and nylon filters. The absorption of SO_2(g) by nylon, paper, or the various sorbent beds does not interfere with the ion chromatographic determination of monomethyl sulfate in aqueous extracts of the samples. It interferes only with the determination of the fraction of monomethyl sulfate or dimethyl sulfate converted to sulfate during sampling and/or extraction.

Table VI. Results of Field Trials for Collection of Gas-Phase Dimethyl Sulfate and Monomethyl Hydrogen Sulfate with XAD-II and Nylon

$[S_T]$,[a] μmol/m³	sampling system	mole ratio to total sulfur × 10⁶ $(CH_3O)_2SO_2$	CH_3OSO_3H	SO_4^{2-}
1990 ± 50	quartz filter	11 ± 5	<5	12000
	glass wool plug	3 ± 4	1 ± 1	7010
	XAD-II bed	87 ± 30	<2	58
	XAD-II bed	6 ± 4	<2	105
	nylon filter	<2	1.5 ± 1.0	39

[a]$[S_T]$ = total concentration in the flue line of all sulfur species collected.

Field Validation Experiments. As indicated by the results given in Table VI, the nylon and XAD-II resin bed collectors performed well in trial experiments in the flue line of a small coal-fired heating plant. Evidence for the artifact collection of SO_2 were evident in these field trials with high total $[SO_2(g)]$. Corrections for SO_2(g) collected were made on the basis of collection in sequential XAD-II resin beds and sequential nylon filters. The data, corrected for SO_2(g) adsorption, indicate that dimethyl sulfate was present at about 0.01% of the SO_2(g) concentration in the sampled flue line. Similar results have been obtained in samples from the flue line of a large coal-fired power plant (*17*). The denuder sampling systems were not tested in the field validation reported here because the sampled concentrations were too low, but both gas-phase dimethyl sulfate and monomethyl hydrogen sulfate have been shown to be present by using the denuder sampling systems in experiments in the Los Angeles basin where concentrations are higher (*12*).

Summary

Various denuder and sorbent collection procedures for the collection of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate have been tested in the laboratory. The methyl sulfates used in these studies were either purified or synthesized by us. The expected diffusion coefficients for the gas-phase species were obtained in the

laboratory experiments by using diffusion denuders. The procedures described allow the construction of a variety of sampling systems for the collection and determination of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate. The combination of these sampling configurations allows the collection and determination of each of the anayltes of interest by two independent procedures. The sampling procedures have been validated in field experiments reported here and in studies completed in the Los Angeles basin (*12*).

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Registry No. $K(CH_3O)SO_3$, 562-54-9; XAD-II, 54596-43-9; PVA, 26336-38-9; PEI, 9002-98-6; PVP, 9003-47-8; H_2SO_4, 7664-93-9; $(CH_3O)_2SO_2$, 77-78-1; $(CH_3O)SO_3H$, 75-93-4; Melamine, 108-78-1.

Literature Cited

(1) Eatough, D. J.; Arthur, R. J.; Eatough, N. L.; Hill, M. W.; Mangelson, N. F.; Richter, B. E.; Hansen, L. D.; Cooper, J. A. *Environ. Sci. Technol.* **1984**, *18*, 855–859.
(2) Eatough, D. J.; Hansen, L. D., unpublished results reported to W. E. Wilson, U.S. EPA, 1982.
(3) Eatough, D. J.; Lee, M. L.; Later, D. W.; Richter, B. E.; Eatough, N. L.; Hansen, L. D. *Environ. Sci. Technol.* **1981**, *15*, 1502–1506.
(4) Eatough, D. J. "Determination of Sulfur Speciation in Industrial Aerosols in an SO_2 Rich Environment"; progress report for U.S. DOE Contract No. DE-AC02-80EV10405, July 30, 1981.
(5) Lee, M. L.; Later, D. W.; Rollins, D. K.; Eatough, D. J.; Hansen, L. D. *Science (Washington, D.C.)* **1980**, *207*, 186–188.
(6) Hoffman, G. R. *Mutat. Res.* **1980**, *75*, 63–129.
(7) Tan, E.-L.; Brimer, P. A.; Schenley, R. L.; Shie, A. W. *J. Toxicol. Environ. Health* **1983**, *11*, 373–379.
(8) Durham, J. L.; Spiller, L.; Eatough, D. J.; Hansen, L. D. "Dimethyl and Methyl Hydrogen Sulfate in the Atmosphere"; APCA Specialty Conference, Research Triangle Park, NC, March 12–14, 1984.
(9) Durham, J. L.; Spiller, L.; Eatough, D. J.; Hansen, L. D. "Evidence for Gaseous Monomethyl Hydrogen Sulfate or Dimethyl Sulfate in Riverside, California"; presented at the ACS Meeting, St. Louis, MO, Oct 1982.
(10) Slanina, J.; Schoonebeck, C. A. M.; Klockow, D.; Niessner, R., submitted for publication.
(11) Gautney, J.; Kim, Y. K.; Hatfield, J. D. *J. Air Pollut. Control Assoc.* **1982**, *32*, 260–265.
(12) Eatough, D. J.; White, V. F.; Hansen, L. D.; Eatough, N. L.; Cheney, J. L. *Environ. Sci. Technol.*, preceding paper in this issue.
(13) Gormley, P. G.; Kennedy, M. *Proc. R. Irish Acad. Sect. A* **1949**, *52*, 163–169.
(14) Durham, J. L.; Spiller, L. "Measurement of Gaseous, Volatile, and Nonvolatile Inorganic Nitrate in Riverside, California"; presented at the ACS Meeting, St. Louis, MO, Oct 1982.
(15) Japar, S. M.; Brachaczek, W. W. *Atmos. Environ.* **1984**, *18*, 2479–2482.
(16) Anlauf, K. G.; Fellin, P.; Wiebe, H. A. "Characterization of Several Integrative Sampling Methods for Atmospheric Particulates, Nitric Acid and Sulphur Dioxide"; report to Environment Canada, CSC 110.J354, Concord Scientific Corporation, Downsview, Ontario, Jan 1984.
(17) Eatough, D. J.; White, V. F.; Hansen, L. D.; Cheney, J. L., unpublished results, Brigham Young University, 1984.

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